

Method 1688

**Total Kjeldahl Nitrogen in Water and Biosolids by Automated
Colorimetry with Preliminary Semi-automatic Digestion**

**DRAFT
January 2001**

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Acknowledgments

This method was prepared under the direction of William A. Telliard of the U.S. Environmental Protection Agency's (EPA's) Office of Water (OW), Engineering and Analysis Division (EAD). The method was prepared under EPA Contract 68-C-98-139 by DynCorp Information and Enterprise Technology.

Disclaimer

This draft method has been reviewed and approved for publication by the Analytical Methods Staff within the Engineering and Analysis Division of EPA. Mention of trade names or commercial products does not constitute endorsement or recommendation for use. EPA plans further validation of this draft method. The method may be revised following validation to reflect results of the study. This method version contains minor editorial changes to the November 1999 version.

EPA welcomes suggestions for improvement of this method. Suggestions and questions concerning this method or its application should be addressed to:

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Note: This method is performance based. The laboratory is permitted to omit any step or modify any procedure provided that all performance requirements in this method are met. The laboratory may not omit any quality control analyses. The terms "shall," "must," and "may not" define procedures required for producing reliable results. The terms "should" and "may" indicate optional steps that may be modified or omitted if the laboratory can demonstrate that the modified method produces results equivalent or superior to results produced by this method.

Method 1688

Total Kjeldahl Nitrogen in Water and Biosolids by Automated Colorimetry with Preliminary Semi-Automatic Digestion

1.0 Scope and Application

- 1.1 This method describes procedures for the determination of total kjeldahl nitrogen (TKN) and/or organic nitrogen in drinking, ground, and surface water; domestic and industrial waste; and biosolids (municipal sewage sludge). Automatic digestion of the sample is followed by analysis using automated colorimetry. This method is based on U.S. Environmental Protection Agency (EPA) Method 351.2: *Nitrogen, Kjeldahl (Colorimetric; Semi-Automated Digester, AAI)* (Reference 16.1). This method is associated with Method 1691: *Municipal Biosolids Sampling Guidance* (Reference 16.2).
- 1.2 This method is to be used in EPA's data gathering and monitoring programs under the Clean Water Act, the Resource Conservation and Recovery Act, the Comprehensive Environmental Response, Compensation, and Liability Act, the Solid Waste Disposal Act, and the Safe Drinking Water Act.
- 1.3 Method detection limits and minimum levels for TKN have not been formally established for this draft method. These values will be determined during the validation of the method.
- 1.4 This method is performance based. The laboratory is permitted to omit any step or modify any procedure, provided that all performance requirements in this method are met. Requirements for establishing method equivalency are given in Section 9.1.2.
- 1.5 Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedures in Section 9.2.

2.0 Summary of Method

- 2.1 The kjeldahl nitrogen in the sample is first converted to ammonia by metal-catalyzed acid digestion using a block heater/digester unit. The resulting ammonia is then separated from the sample by distillation. A procedure is given for removal of the ammonia present in the sample prior to digestion. A sample so treated then gives a result of organic nitrogen after digestion/distillation.
- 2.2 The ammonia concentration of the digestate is determined by automated colorimetric measurement of indophenol blue, which is formed when ammonia reacts with alkaline phenol and hypochlorite.
- 2.3 Cupric sulfate has been substituted for the historically-used mercuric sulfate due to toxicity and waste disposal problems associated with mercury.
- 2.4 Quality is assured through calibration and testing of the analytical instruments and testing of the sample preparation.

3.0 Definitions

Definitions for terms used in this method are given in Section 18.

4.0 Interferences

- 4.1** Nitrate in large quantities (>10 mg/L) will oxidize ammonia produced by the digestion and cause a negative bias. No known method exists to prevent this interference, but its effect can be predicted on the basis of preliminary nitrate determination of the sample.
- 4.2** Inorganic salts or solids will increase the temperature at which the digestion takes place, and digestion temperatures in excess of 400°C will cause pyrolytic loss of nitrogen. If high salt/solid content is suspected, addition of extra volumes of sulfuric acid will stabilize the temperature. Approximately 1 mL H₂SO₄ per g of salt/solid will preserve the proper ratio.
- 4.3** Large amounts of organic matter can consume the acid in the digestion reagent, causing the temperature of the digestion to rise above 400°C. Addition of 10 mL H₂SO₄ per 3000 mg COD will prevent this interference. Monitor digestion temperature and pH if this correction is used.
- 4.4** Residual chlorine, if present, must be removed by pretreatment of the sample with sodium thiosulfate before digestion/distillation. Typically, this will be necessary if the sample contains free water or is aqueous.
- 4.5** Nitrogen occurring in certain organic compounds will not be measured by this method. These compounds include those having nitrogen in the following forms: azide, azine, azo, hydrazone, nitrate, nitrite, nitrile, nitro, nitroso, oxime, and semicarbazone.

5.0 Safety

- 5.1** The toxicity or carcinogenicity of reagents used in this method has not been fully established. Each chemical and environmental sample should be regarded as a potential health hazard and exposure should be minimized. Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDS) should be available to all personnel involved in the chemical analysis. Additional information on laboratory safety can be found in Reference 16.3.
- 5.2** If samples originate from a highly contaminated area, appropriate sample handling procedures must be followed to minimize worker exposure.
- 5.3** All personnel handling environmental samples known to contain or to have been in contact with human waste should be immunized against known disease causative agents.

6.0 Apparatus and Equipment

NOTE: *Brand names, suppliers, and part numbers are for illustration only, and no endorsement is implied. Equivalent performance may be achieved using apparatus and materials other than those specified here. Meeting the performance requirements of this method is the responsibility of the sampling team and laboratory.*

6.1 Digestion

6.1.1 Digester tubes, 50 mL.

- 6.1.2** Automatic block type heating unit, with low and high range settings and timers.
- 6.2** Colorimetric analysis—Automated analytical equipment with the capability of delivering the reagents specified in Figure 1 at the specified rates, and with a colorimeter capable of measuring at 630-660 nm.
- 6.3** General equipment
- 6.3.1** Analytical balance, capable of weighing to 0.001 g (1 mg).
- 6.3.2** Hot plate or other heating apparatus.
- 6.3.3** Boiling chips or glass beads
- 6.3.4** Clean dish or watchglass

7.0 Reagents and Consumable Materials

- 7.1** All water and reagents used in this method must be free of ammonia.
- 7.1.1** Ammonia-free reagent water—Ammonia-free water can be prepared by passing reagent water through an ion-exchange column containing a mixture of both strongly acidic cation and strongly basic anion exchange resins. When necessary, regenerate the column according to the manufacturer's instructions.
- 7.1.2** All reagents should be ACS Reagent Grade or better.
- 7.2** Sulfuric acid
- 7.2.1** 5N Sulfuric acid (H_2SO_4)—Carefully add 139 mL of concentrated H_2SO_4 to approximately 500 mL reagent water. Cool to room temperature and dilute to 1 L.
- 7.2.2** 0.04N Sulfuric acid—Carefully add 4 mL of 5N H_2SO_4 (Section 7.2.1) to approximately 300 mL reagent water. Cool to room temperature and dilute to 500 mL.
- 7.3** Sodium hydroxide solutions

CAUTION: *Considerable heat is generated upon dissolution of sodium hydroxide in water. It may be advisable to cool the container in an ice bath when preparing sodium hydroxide solutions.*

- 7.3.1** 0.1N Sodium hydroxide (NaOH)—Dissolve 4.0 g NaOH in reagent water, cool, and dilute to 1 L.
- 7.3.2** 6N Sodium hydroxide—Dissolve 240 g NaOH in reagent water, cool, and dilute to 1 L.

- 7.3.3** 1N Sodium hydroxide—Dissolve 40 g NaOH in reagent water, cool, and dilute to 1 L.
- 7.4** Borate buffer
- 7.4.1** 0.025M Sodium tetraborate—Dissolve 5 g anhydrous sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) or 9.5 g sodium tetraborate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in reagent water and dilute to 1 L.
- 7.4.2** Add 88 mL of 0.1N NaOH solution (Section 7.3.1) to 500 mL 0.025M $\text{Na}_2\text{B}_4\text{O}_7$ (Section 7.4.1) and dilute to 1 L with reagent water.
- 7.5** Sodium phenate—Using a 1-L Erlenmeyer flask, dissolve 83 g phenol in 500 mL reagent water. Add 32 g NaOH cautiously and in small increments while agitating the flask. Periodically cool the flask under running water. When cool, dilute to 1 L.
- 7.6** Sodium hypochlorite solution—Dilute 250 mL of a bleach solution containing 5.25% NaOCl (such as “Clorox”) to 500 mL. Available chlorine level should approximate 2-3%. Since “Clorox” is a proprietary product, its formulation is subject to change. The analyst must remain alert to detecting any variation in this product significant to its use in this procedure. Due to the instability of bleach, storage over an extended period should be avoided.
- 7.7** 5% Disodium ethylenediamine-tetraacetate (EDTA)—Dissolve 50 g EDTA (disodium salt) and approximately six pellets NaOH in 1 L of reagent water.
- 7.8** 0.05% Sodium nitroprusside—Dissolve 0.5 g of sodium nitroprusside ($\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$) in 1 L reagent water.
- 7.9** Blank sand—Bake 500 g diatomaceous earth or clean sand at 400°C for eight hours. Cool and store in a glass container with a sealing lid.
- 7.10** Ammonia standards
- 7.10.1** Ammonia stock solution (1000 mg/L $\text{NH}_3\text{-N}$)—Dissolve 0.382 g of anhydrous ammonium chloride (NH_4Cl) in reagent water and dilute to 100 mL in a volumetric flask. NH_4Cl should be dried at 105°C prior to use.
- 7.10.2** Ammonia working standard (10 mg/L $\text{NH}_3\text{-N}$)—In a volumetric flask, dilute 10 mL of ammonia stock solution (Section 7.10.1) to 1 L.
- 7.11** Digestion reagent—Dissolve 134 g potassium sulfate (K_2SO_4) and 7.3 g cupric sulfate (CuSO_4) in 800 mL reagent water. Slowly add 134 mL conc. sulfuric acid. Cool and dilute solution to 1 L. Mix well. Store the solution at room temperature.
- 7.12** Sodium hydroxide-sodium thiosulfate solution—Dissolve 500 g NaOH and 25 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ in reagent water and dilute to 1 L.
- 7.13** Nicotinic acid standard 100 mg/L organic N—Dissolve 21.637 g nicotinic acid ($\text{C}_6\text{H}_5\text{NO}_2$) in approximately 150 mL reagent water. Dilute to 200 mL.

- 7.14** Dechlorinating reagent—Dissolve 0.35 g sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$) in reagent water and dilute to 100 mL. One mL of this reagent will neutralize 1 mg/L of residual chlorine in a 500 mL sample aliquot.
- 7.15** Quality control sample (QCS)—A prepared quality control sample from a standards vendor (ERA catalog # 545, or equivalent).

8.0 Sample Collection, Preservation and Storage

- 8.1** Ammonia is a pervasive contaminant. Minimize exposure of samples to air as much as possible.
- 8.2** A sufficient volume of sample for analysis must be collected using the procedures found in Reference 16.2 for biosolids samples and Reference 16.4 for water and wastewater samples.
- 8.3** Ammonia can be formed or lost during storage due to biological activity or lost by volatilization or oxidation. The following preservation procedures will help prevent significant changes in the analyte concentration.
- 8.3.1** Samples should be collected in wide mouth jars with a minimum of air space above them.
- 8.3.2** Aqueous samples or samples that contain free water
- 8.3.2.1** Samples should be checked for residual chlorine and treated with sodium thiosulfate, if necessary, during collection.
- 8.3.2.2** Samples should be preserved with 2 mL concentrated H_2SO_4 and cooled to 4°C as soon as possible after collection. The holding time for samples should not exceed 28 days from sampling.
- 8.3.3** If the sample contains no free water or is solid, the sample should be cooled to 4°C as soon as possible after collection. The holding time for samples should not exceed 28 days from sampling.
- 8.4** Collect a separate sample for total solids determination (Appendix A). The holding time for total solids determination is seven days.

9.0 Quality Control

- 9.1** Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the ongoing analysis of laboratory reagent blanks, precision and recovery standards, and matrix-spiked samples as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data thus generated. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.
- 9.1.1** The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2.

9.1.2 In recognition of advances that are occurring in analytical technology, the analyst is permitted certain options to improve separations or lower the costs of measurements, provided that all performance specifications are met. Changes that degrade method performance are not allowed. If an analytical technique other than the technique specified in this method is used, that technique must have a specificity equal to or better than the specificity of the techniques in this method for TKN in the sample of interest. Specificity is defined as producing results equivalent to the results produced by this method for analytical standards (Section 9.4) and, where applicable, environmental samples (Section 9.5), and as meeting all of the QC criteria stated in this method.

9.1.2.1 Each time a modification is made to this method, the analyst is required to repeat the IPR test in Section 9.2.2 to demonstrate that the modification produces results equivalent to or better than results produced by this method. If the detection limit of the method will be affected by the modification, the analyst must demonstrate that the MDL (40 CFR part 136, appendix B) is less than or equal to the MDL in this method or one-third the regulatory compliance level, whichever is higher. The tests required for this equivalency demonstration are given in Section 9.1.2.2.4.

9.1.2.2 The laboratory is required to maintain records of modifications made to this method. These records include the following, at a minimum:

9.1.2.2.1 The names, titles, addresses, and telephone numbers of the analyst(s) who performed the analyses and modification, and of the quality control officer who witnessed and will verify the analyses and modification.

9.1.2.2.2 A listing of pollutant(s) measured (TKN).

9.1.2.2.3 A narrative stating reason(s) for the modification.

9.1.2.2.4 Results from all quality control (QC) tests comparing the modified method to this method, including:

- (a) Calibration (Section 10).
- (b) Calibration verification (Section 9.6).
- (c) Initial precision and recovery (Section 9.2.2).
- (d) Analysis of blanks (Section 9.3).
- (e) Accuracy assessment (Sections 9.5 and 9.7).
- (f) Ongoing precision and recovery (Section 9.4).
- (g) Method detection limit (Section 9.2.1)

9.1.2.2.5 Data that will allow an independent reviewer to validate each determination by tracing the instrument output (weight, absorbance, or other signal) to the final result. These data are to include:

- (a) Sample numbers and other identifiers.
- (b) Sample preparation dates.
- (c) Analysis dates and times.
- (d) Analysis sequence/run chronology.

- (e) Sample weight or volume.
- (f) Dry weight ratio (solid and semi-solid samples only; Appendix A).
- (g) Distillate solution volume.
- (h) Make and model of analytical balance and weights traceable to NIST.
- (i) Copies of logbooks, printer tapes, and other recordings of raw data.
- (j) Data system outputs, and other data to link the raw data to the results reported.

9.1.3 Analyses of laboratory blanks are required to demonstrate freedom from contamination. The procedures and criteria for blank analyses are described in Section 9.3

9.1.4 Analyses of ongoing precision and recovery samples are required to demonstrate that the sample preparation and analysis are within the specified limitations. The procedure and criteria for OPR sample analysis are described in Section 9.4.

9.1.5 Analyses of matrix spike and matrix spike duplicate samples are required to demonstrate method accuracy and precision, and to monitor interferences caused by the sample matrix. The procedure and criteria for spiking are described in Section 9.5.

9.1.6 Analyses of calibration verification standards are required to demonstrate accuracy and stability of the initial calibration. The procedure and criteria for calibration verification analyses are described in Section 9.6.

9.1.7 Analyses of quality control samples (QCS) are required to demonstrate the accuracy of the calibration standards and the analytical system. The procedure and criteria for the QCS sample analyses are described in Section 9.7.

9.2 Initial demonstration of laboratory capability—The initial demonstration of laboratory capability is used to characterize laboratory performance and method detection limits. The MDL and IPR for solid samples should be determined using blank sand as a reference matrix. The MDL and IPR for aqueous samples should be determined using reagent water as a reference matrix.

9.2.1 Method detection limit (MDL)—The MDL should be established for TKN according to the procedures at 40 CFR part 136, appendix B (Reference 16.5). First, spike a reference matrix with nicotinic acid (Section 7.13) at a concentration one to five times the estimated detection limit. To determine the MDL, take seven replicate aliquots of the spiked reference matrix and process each aliquot through each step of the analytical method. Perform all calculations and report the concentration values in the appropriate units. Aqueous and/or solid method detection limits should be determined every year or whenever a modification to the method or analytical system is made that will affect the MDL.

9.2.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

9.2.2.1 Prepare four spiked samples as detailed in Section 9.4. Using the procedures in Section 11, prepare and analyze these spiked samples for TKN.

- 9.2.2.2** Using the results of the set of four analyses, compute the average percent recovery (X) and the standard deviation (s) of the percent recovery for TKN.
- 9.2.2.3** Compare s and X with the corresponding limits for initial precision and recovery in Table 1. If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem, and repeat the test.
- 9.3** Laboratory blanks—Laboratory blanks are analyzed to demonstrate freedom from contamination. Aqueous samples should be run with an aqueous blank, and solid samples should be run with a solid blank.
- 9.3.1** Prepare and analyze a laboratory blank initially (i.e., with the tests in Section 9.2) and with each analytical batch. The blank must be subjected to the same procedural steps as a sample, and will consist of 250 mL of ammonia-free reagent water (aqueous blank) or 5 g aliquot of blank sand in 250 mL of ammonia-free reagent water (solid blank).
- 9.3.2** If material is detected in the aqueous or solid blank at a concentration greater than the aqueous or solid MDL (Section 1.3), analysis of samples is halted until the source of contamination is eliminated and a blank shows no evidence of contamination. All samples must be associated with an uncontaminated laboratory blank before the results may be reported for regulatory compliance purposes.
- 9.4** Ongoing precision and recovery (OPR)—The laboratory must analyze at least one ongoing precision and recovery sample with each analytical batch. A solid OPR should be run with solid samples, and an aqueous OPR should be run with aqueous samples. An aqueous OPR is prepared by spiking reagent water with nicotinic acid standard (Section 7.13) at a concentration so that the concentration of TKN in the OPR is one to five times the ML. A solid OPR is prepared by mixing 5 g of blank sand with 250 mL reagent water and spiking with nicotinic acid standard so that the concentration of TKN in the OPR is one to five times the ML. The spiked aliquot is carried through the entire analytical process (Section 11). Calculate accuracy as percent recovery. If the recovery of the analyte falls outside the control limits in Table 1, the system performance is unacceptable, and the source of the problem should be identified and resolved before continuing analyses.
- 9.5** Matrix spike and matrix spike duplicates (MS/MSD)—To assess the performance of the method on a given sample matrix, the laboratory must spike, in duplicate, a minimum of 10% (one sample in 10) of the samples from a given sampling site or, if for compliance monitoring, from a given discharge. Blanks may not be used for MS/MSD analysis.
- 9.5.1** The concentration of the MS and MSD shall be determined as follows:
- 9.5.1.1** If, as in compliance monitoring, the concentration of analytes in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit or at 1-5 times the background concentration of the sample, whichever is greater.

9.5.1.2 If the concentration of TKN in a sample is not being checked against a regulatory concentration limit, the spike shall be at 1-5 times the background concentration.

9.5.1.3 For solid and sludge samples, the concentration added should be expressed as mg/kg and is calculated for a one gram aliquot by multiplying the added analyte concentration (mg/L) in solution by the conversion factor 100 (mg/L x 0.1L/0.001kg = 100).

9.5.2 Assessing spike recovery

9.5.2.1 To determine the background concentration, analyze one sample aliquot from each set of 10 samples from each site or discharge according to the procedure in Section 11. If the expected background concentration is known from previous experience or other knowledge, the spiking level may be established a priori.

9.5.2.2 Prepare the MS/MSD samples by adding the appropriate concentration of nicotinic acid standard (Section 7.13) to two sample aliquots. Analyze the MS/MSD aliquots as described in Section 11 to determine the concentration of TKN in the samples after spiking.

9.5.3 Calculate the percent recovery (P) and relative percent difference (RPD) of the two matrix spike samples for the analyte, corrected for the background concentration measured in the sample, and compare these values to the control limits given in Table 1. Percent recovery is calculated in units appropriate to the matrix, using Equation 1. RPD is calculated using Equation 2.

Equation 1

$$\text{percent recovery} = \frac{(C_s - C_b)}{S} * 100$$

where: C_s = Measured sample concentration after spiking
 C_b = Measured sample background concentration
 S = known concentration of the spike

Equation 2

$$\text{RPD} = \frac{(|D_1 - D_2|)}{(D_1 + D_2)} * 200$$

where: D_1 = concentration TKN of MS sample
 D_2 = concentration TKN of MSD sample

9.5.4 If the percent recovery or the RPD of the analyte in the MS/MSD samples falls outside the designated range, and the laboratory performance on the OPR for the analyte is within the specified limits (Table 1), the recovery problem encountered with the MS/MSD sample is judged to be matrix-related instead of method-related.

9.5.5 Recovery for samples should be assessed and records maintained.

9.5.5.1 After the analysis of five samples of a given matrix type (river water, lake water, etc.) for which the results pass the tests in Section 9.5.3, compute the average percent recovery (R) and the standard deviation of the percent recovery (SR) for the analyte(s). Express the accuracy assessment as a percent recovery interval from $R-2SR$ to $R+2SR$ for each matrix. For example, if $R=90\%$ and $SR=10\%$ for five analyses of river water, the accuracy interval is expressed as 70-110%.

9.5.5.2 Update the accuracy assessment for each matrix regularly (e.g., after each five to ten new measurements).

9.6 Calibration verification (CV)—The laboratory must analyze a calibration verification standard before running any samples and once per ten analyses thereafter. The CV should be prepared at a concentration that is at or near the midpoint of the calibration curve. The source of the CV standard should be different from the source used to prepare the calibration standards. If a different compound is used for the CV stock, the amount weighed will have to be adjusted according to the ratio of ammonia-nitrogen compound atomic weight to the molecular weight. Results of the CV analysis should be evaluated according to the specifications in Table 1. If the CV does not meet acceptance criteria, the problem must be identified and corrected, including possible recalibration of the instrument.

9.7 Quality control sample (QCS)—It is suggested that the laboratory analyze a QCS with each day's distillations, or every twelve hours, whichever is more frequent. The results of the QCS analysis should be evaluated according to the manufacturer's specifications.

10.0 Calibration and Standardization

10.1 Calibrate the colorimeter with a minimum of ten standards that cover the expected range of the samples and a blank. If the autoanalyzer is linked to a data system, follow the manufacturer's instructions for calibration. Alternatively, prepare a calibration graph relating absorbance to the concentration of TKN, or develop a weighted linear regression formula from the calibration data using concentration versus absorbance. If the correlation coefficient falls below 0.995, check the system for faults, correct them if found, and reanalyze the calibration standards.

10.2 Preparation of calibration curve—Prepare the standards (Table 2) and analyze them according to the procedure in Section 11.2, beginning with the lowest standard. It is not necessary to digest the calibration standards

10.3 An OPR run after the calibration must be within the specified limits (Table 1). Unacceptable OPR results require corrective action before analysis of samples may continue; they may indicate problems with the digestion procedure.

- 10.4** Balance calibration—Calibrate the analytical balance at 2 mg and 1000 mg using class “S” weights. The calibration shall be within $\pm 10\%$ at 2 mg and $\pm 0.5\%$ at 1000 mg. If values are not within these limits, recalibrate the balance.

11.0 Procedure

11.1 Digestion

11.1.1 Sample preparation

11.1.1.1 Solid samples—Thoroughly homogenize the sample. Weigh 5 g of sample in a clean dish or watchglass, transfer to the 50 mL digester tube with reagent water, and add a few boiling chips or glass beads. Bring the volume up to 20 mL with reagent water.

11.1.1.2 Aqueous samples—Mix the sample thoroughly. Transfer 20 mL of sample to the 50 mL tube and add a few boiling chips or glass beads.

11.1.2 Carefully add 5 mL digestion reagent (7.11) to each tube. Set the block digester to manual mode and set low and high temperature to 160°C. Preheat the unit for 30 minutes. Cover the top of each tube with a small square of aluminum foil, and place them in the digester. Set the low temperature timer for one hour. Set the high temperature at 380°C, and set the high temperature timer for 2½ hours.

11.1.3 Allow the tubes to cool, then dilute to 25 mL with reagent water.

11.2 Colorimetric analysis

11.2.1 Since the intensity of the color used to quantify the concentration is pH dependent, the acid concentration of the wash water and the standard ammonia solutions should approximate that of the samples.

11.2.2 Set up the autoanalyzer and reagents according to the manufacturer’s instructions, using the information in Figure 1 as a guide.

11.2.3 Allow both colorimeter and recorder (if applicable) to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding reagent water through the sample line.

11.2.4 Switch the sample line from reagent water to the first sample and begin analysis.

11.3 The solid sample dry weight/wet weight ratio must be determined separately (Appendix A).

12.0 Calculations

12.1 Aqueous samples—Compare the absorbance reading for each sample to the calibration curve and determine the sample concentration. Report all values in mg/L to three significant figures.

- 12.2** Solid samples—Compare the absorbance reading for each sample to the calibration curve and determine the sample concentration using Equations 3 and 4. Report all values in mg/kg to three significant figures.

Equation 3

$$TKN \text{ (mg / kg)} = \frac{(C_d)(V_d)(F)1000 \text{ g / kg}}{(W_s)1000 \text{ mL / L}}$$

where: C_d = Concentration of NH₃-N in digestate (mg/L)
 V_d = Volume of digestate collected
 F = Dilution factor (1 if no dilution)
 W_s = Weight of sample distilled (g)

Equation 4

$$TKN \text{ (mg / kg)} = \frac{C_s}{W}$$

where: C_s = Amount of TKN in sample (mg/kg, Equation 3)
 W = Dry weight ratio (Appendix A)

- 12.3** Report all results below the ML as “less than the ML.”

- 12.4** The QC data obtained during the analysis provides an indication of the quality of the sample data and should be provided with the sample results.

13.0 Method Performance

This is a draft method, and is currently undergoing validation. Method performance criteria will be set following the validation of the method.

14.0 Pollution Prevention

- 14.1** Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Many opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, EPA recommends recycling as the next best option. The acids used in this method should be reused as practicable by purifying by electrochemical techniques. The only other chemicals used in this method are the neat materials used in preparing standards. These standards are used in extremely small amounts and pose little threat to the environment when managed properly. Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

- 14.2** For information about pollution prevention that may be applicable to laboratories and research institutions, consult “Less is Better: Laboratory Chemical Management for Waste Reduction,” available from the American Chemical Society’s Department of Government Relations and Science Policy, 1155 16th Street NW, Washington, D.C. 20036, 202/872–4477.

15.0 Waste Management

- 15.1** The laboratory is responsible for complying with all Federal, State, and local regulations governing waste management, particularly hazardous waste identification rules and land disposal restrictions, and for protecting the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required. An overview of requirements can be found in *Environmental Management Guide for Small Laboratories* (EPA 233-B-98-001).
- 15.2** Samples containing strong acids or bases are hazardous and must be either neutralized before being disposed or handled as hazardous waste.

16.0 References

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- 16.2** U.S. Environmental Protection Agency, 1998. Method 1691: Municipal Biosolids Sampling Guidance. Draft, September 1998. Office of Water, Washington, DC.
- 16.3** Sax, N.I. and Lewis, Sr., R.I., Dangerous Properties of Industrial Materials, 5th. ed., Van Nostrand Reinhold, New York, 1989.
- 16.4** U.S. Environmental Protection Agency, 1982. Handbook for Sampling and Sample Preservation of Water and Wastewater. Publ. 600/4-82-029, Environmental Monitoring and Support Lab., U.S. Environmental Protection Agency, Cincinnati, Ohio.
- 16.5** Code of Federal Regulations 40, Ch. 1, Part 136, Appendix B.

17.0 Tables, Diagrams, and Validation Data

Table 1. Quality Control—Sample Acceptance Criteria (To be determined during the method validation study)

| Analyte | Blank limit | IPR recovery (x) limit | IPR precision (s) limit | OPR recovery limit | CV recovery limit | QCS recovery limit |
|---------|-------------|------------------------|-------------------------|--------------------|-------------------|--------------------|
| TKN | | | | | | |

Table 2. The volume of working standard necessary to make the calibration standards in 100 mL volumetric flasks

| Volume of standard (Section 7.10.2) added (mL) | Concentration of calibration standard (mg/L) |
|---|---|
| 0.1 | 0.01 |
| 0.2 | 0.02 |
| 0.5 | 0.05 |
| 1.0 | 0.10 |
| 2.0 | 0.20 |
| 5.0 | 0.50 |
| 8.0 | 0.80 |
| 10.0 | 1.00 |
| 15.0 | 1.50 |
| 20.0 | 2.00 |

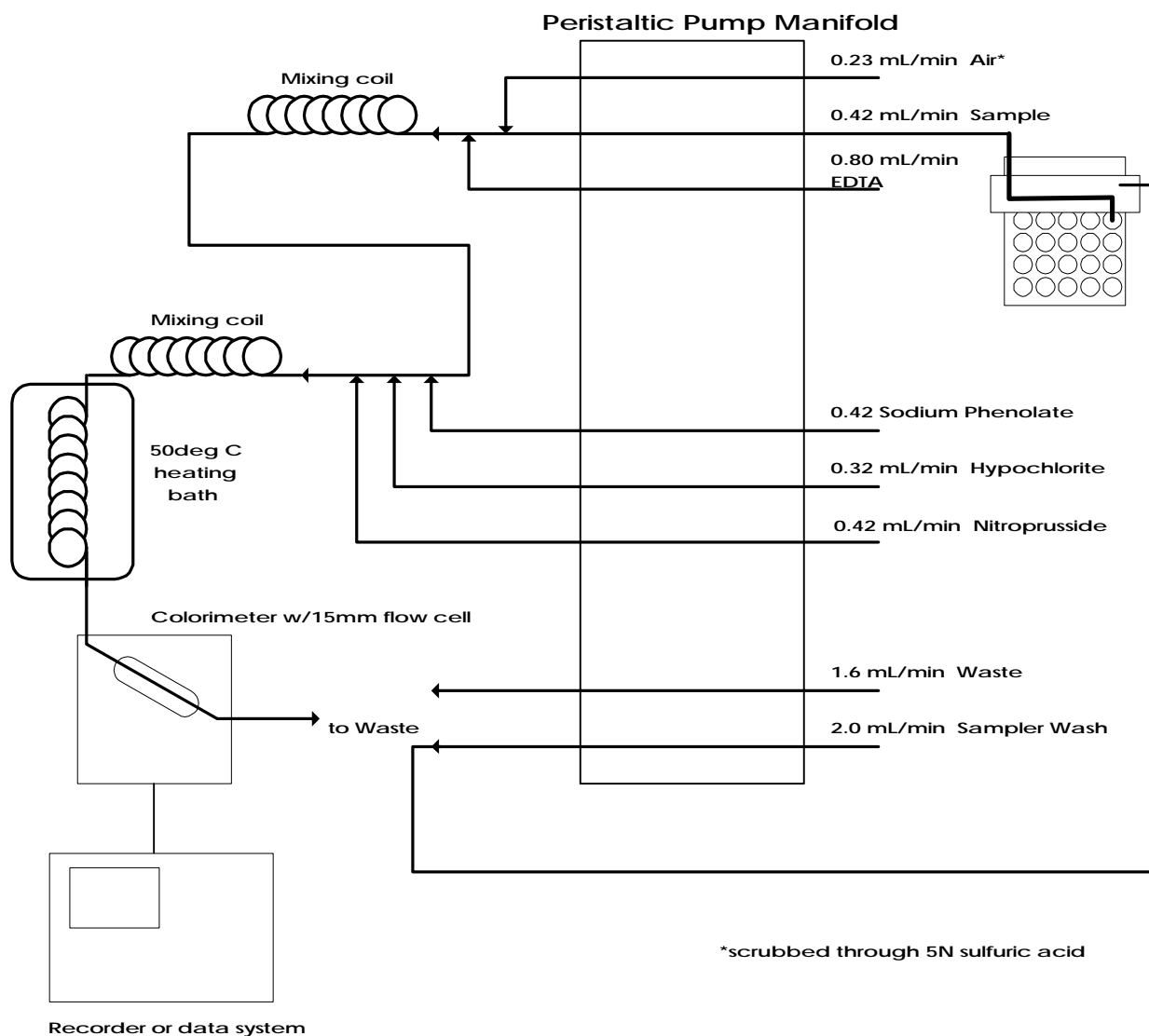


Figure 1. Continuous Flow Diagram

18.0 Glossary of Terms

The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible.

- 18.1 Ammonia-N**—The quantity of nitrogen occurring in the ammonium ion.
- 18.2 Analyte**—A compound or element tested for by the methods referenced in this method.
- 18.3 Analytical Batch**—The set of samples analyzed at the same time, to a maximum of 10 samples.

- 18.4 Apparatus**—The sample container and other containers, filters, filter holders, labware, tubing, pipettes, and other materials and devices used for sample collection or sample preparation, and that will contact samples, blanks, or analytical standards.
- 18.5 Biosolids**—The treated residuals from wastewater treatment that can be used beneficially.
- 18.6 Calibration Standard**—A solution prepared from a dilute mixed standard and/or stock solution and used to calibrate the response of the instrument with respect to analyte concentration
- 18.7 Calibration Verification Standard (CV)**—A solution prepared from a different source than the calibration standards that is used to confirm the accuracy of the instrument’s calibration.
- 18.8 Initial Precision and Recovery (IPR)**—Four aliquots of the OPR standard analyzed to establish the ability to generate acceptable precision and accuracy. IPR is performed before a method is used for the first time and any time the method or instrumentation is modified.
- 18.9 Kjeldahl Nitrogen (TKN)**—the sum of ammonia-nitrogen and organic nitrogen.
- 18.10 Laboratory Blank**—An aliquot of reagent water that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with samples. The laboratory blank is used to determine if method analytes or interferences are present in the laboratory environment, the reagents, or the apparatus (Section 9.3).
- 18.11 Matrix Spike (MS) and Matrix Spike Duplicate (MSD)**—Aliquots of an environmental sample to which known quantities of the method analytes are added in the laboratory. The MS and MSD are analyzed exactly like a sample. Their purpose is to quantify the bias and precision caused by the sample matrix. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the MS and MSD corrected for background concentrations (Section 9.5).
- 18.12 May**—This action, activity, or procedural step is optional.
- 18.13 May Not**—This action, activity, or procedural step is prohibited.
- 18.14 Method Detection Limit (MDL)**—The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero (Section 9.2.1).
- 18.15 Minimum Level (ML)**—The lowest level at which the entire analytical system gives a recognizable signal and acceptable calibration point.
- 18.16 Must**—This action, activity, or procedural step is required.
- 18.17 Ongoing Precision and Recovery (OPR) Standard**—A laboratory blank spiked with known quantities of the method analytes. The OPR is analyzed exactly like a sample. Its purpose is to determine whether the methodology is in control and to assure that the results produced by the laboratory remain within the method-specified limits for precision and accuracy (Section 9.4).

- 18.18 Organic Nitrogen**—nitrogen present in organic molecules in the trinegative oxidation state.
- 18.19 Reagent Water**—Water demonstrated to be free from the method analytes and potentially interfering substances at the MDL for the method.
- 18.20 Sewage Sludge**—Sewage sludge is solid, semi-solid, or liquid residue generated during the treatment process of domestic sewage in a treatment works. Sewage sludge includes but is not limited to, domestic septage; scum or solids removed in primary, secondary, or advanced wastewater treatment processes; and a material derived from sewage sludge. Sewage sludge does not include ash generated during the firing of sewage sludge in a sewage sludge incinerator or grit and screenings generated during preliminary treatment of domestic sewage in a treatment works.
- 18.21 Shall**—This action, activity, or procedural step is required.
- 18.22 Should**—This action, activity, or procedural step is suggested but not required.
- 18.23 Stock Standard Solution**—A solution containing one or more method analytes that is prepared using a reference material traceable to EPA, the National Institute of Science and Technology (NIST), or a source that will attest to the purity and authenticity of the reference material.

Appendix A: Total Solids in Solids and Biosolids

1.0 Scope and Application

- 1.1 This procedure is applicable to the determination of total solids in such solid and semisolid samples as soils, sediments, biosolids (municipal sewage sludge) separated from water and wastewater treatment processes, and sludge cakes from vacuum filtration, centrifugation, or other sludge dewatering processes.
- 1.2 This procedure is taken from EPA Method 1684: *Total, Fixed, and Volatile Solids in Water, Solids and Biosolids*.
- 1.3 Method detection limits (MDLs) and minimum levels (MLs) have not been formally established for this draft procedure. These values will be determined during the validation of Method 1684.
- 1.4 This procedure is performance based. The laboratory is permitted to omit any step or modify any procedure (e.g. to overcome interferences, to lower the cost of measurement), provided that all performance requirements in this procedure are met. Requirements for establishing equivalency are given in Section 9.1.2 of Method 1688.
- 1.5 Each laboratory that uses this procedure must demonstrate the ability to generate acceptable results using the procedure in Section 9.2 of this appendix.

2.0 Summary of Method

- 2.1 Sample aliquots of 25-50 g are dried at 103°C to 105°C to drive off water in the sample.
- 2.2 The mass of total solids in the sample is determined by comparing the mass of the sample before and after each drying step.

3.0 Definitions

- 3.1 Analytical batch—The set of samples analyzed at the same time, to a maximum of 10 samples. Each analytical batch of 10 or fewer samples must be accompanied by a laboratory blank, an ongoing precision and recovery sample, and a set of duplicate samples, resulting in a minimum of five analyses (1 sample, 1 blank, 1 OPR, and 2 duplicates) and a maximum of 14 samples.
- 3.2 Total Solids—The residue left in the vessel after evaporation of liquid from a sample and subsequent drying in an oven at 103°C to 105°C.
- 3.3 Additional definitions are given in Sections 3.0 and 18.0 of Method 1688.

4.0 Interferences

- 4.1 Sampling, subsampling, and pipeting multi-phase samples may introduce serious errors (Reference 16.1). Make and keep such samples homogeneous during transfer. Use special handling to ensure

sample integrity when subsampling. Mix small samples with a magnetic stirrer. If visible suspended solids are present, pipet with wide-bore pipets. If part of a sample adheres to the sample container, intensive homogenization is required to ensure accurate results. When dried, some samples form a crust that prevents evaporation; special handling such as extended drying times are required to deal with this. Avoid using a magnetic stirrer with samples containing magnetic particles.

- 4.2** The temperature and time of residue drying has an important bearing on results (Reference 16.1). Problems such as weight losses due to volatilization of organic matter, and evolution of gases from heat-induced chemical decomposition, weight gains due to oxidation, and confounding factors like mechanical occlusion of water and water of crystallization depend on temperature and time of heating. It is therefore essential that samples be dried at a uniform temperature, and for no longer than specified. Each sample requires close attention to desiccation after drying. Minimize the time the desiccator is open because moist air may enter and be absorbed by the samples. Some samples may be stronger desiccants than those used in the desiccator and may take on water. If uptake of water by a sample is suspected, the operator should weigh the sample to see if it gains weight while in the desiccator. If the sample is indeed taking on water, then a vacuum desiccator should be used.
- 4.3** Residues dried at 103°C to 105°C may retain some bound water as water of crystallization or as water occluded in the interstices of crystals. They lose CO₂ in the conversion of bicarbonate to carbonate. The residues usually lose only slight amounts of organic matter by volatilization at this temperature. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow.
- 4.4** Results for residues high in oil or grease may be questionable because of the difficulty of drying to constant weight in a reasonable time.
- 4.5** The determination of total solids is subject to negative error due to loss of ammonium carbonate and volatile organic matter during the drying step at 103°C to 105°C. Carefully observe specified ignition time and temperature to control losses of volatile inorganic salts if these are a problem.

5.0 Safety

- 5.1** Refer to Section 5.0 of Method 1688 for safety precautions

6.0 Equipment and Supplies

NOTE: *Brand names, suppliers, and part numbers are cited for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and materials other than those specified here, but demonstration of equivalent performance that meets the requirements of this method is the responsibility of the laboratory.*

- 6.1** Evaporating Dishes—Dishes of 100-mL capacity. The dishes may be made of porcelain (90-mm diameter), platinum, or high-silica glass.
- 6.2** Watch glass—Capable of covering the evaporating dishes (Section 6.1).

- 6.3 Steam bath for evaporation of liquid samples.
- 6.4 Desiccator—Moisture concentration in the desiccator should be monitored by an instrumental indicator or with a color-indicator desiccant.
- 6.5 Drying oven—Thermostatically-controlled, capable of maintaining a uniform temperature of 103°C to 105°C throughout the drying chamber.
- 6.6 Analytical balance—Capable of weighing to 0.1 mg for samples having a mass up to 200 g.
- 6.7 Reference weights—2 mg, 1000 mg, and 50 g class “S” weights.
- 6.8 Container handling apparatus—Gloves, tongs, or a suitable holder for moving and handling hot containers after drying.
- 6.9 Sample handling apparatus—Spatulas, spoonulas, funnels, or other equipment for transfer and manipulation of samples.
- 6.10 Bottles—Glass or plastic bottles of a suitable size for sample collection.
- 6.11 Rubber gloves (Optional).
- 6.12 No. 7 Cork borer (Optional).
- 6.13 Dessicant (Optional).

7.0 Reagents and Standards

- 7.1 Reagent water—Deionized, distilled, or otherwise purified water.
- 7.2 Quality control spiking solution—If a commercially available standard can be purchased that contains standard total solids, the laboratory may use that standard. The laboratory may also prepare a spiking solution. One possible recipe is given below for a NaCl-KHP solution.
 - 7.2.1 Dissolve 0.10 g sodium chloride (NaCl) in 500 mL reagent water. Mix to dissolve.
 - 7.2.2 Add 0.10 g potassium hydrogen phthalate (KHP) to the NaCl solution (Section 7.2.1) and mix. If the KHP does not dissolve readily, warm the solution while mixing. Dilute to 1 L with reagent water. Store at 4°C. Assuming 100% volatility of the acid phthalate ion, this solution contains 200 mg/L total solids, 81.0 mg/L volatile solids, and 119 mg/L fixed solids.

8.0 Sample Collection, Preservation, and Storage

- 8.1 Use resistant-glass or plastic bottles to collect sample for solids analysis, provided that the material in suspension does not adhere to container walls. Sampling should be done in accordance with Reference 16.2. Begin analysis as soon as possible after collection because of the impracticality of preserving the sample. Refrigerate the sample at 4°C up to the time of analysis to minimize

microbiological decomposition of solids. Preferably do not hold samples more than 24 hours. Under no circumstances should the sample be held more than seven days. Bring samples to room temperature before analysis.

9.0 Quality Control

9.1 Quality control requirements and requirements for performance-based methods are given in Section 9.1 of Method 1688.

9.2 Initial demonstration of laboratory capability—The initial demonstration of laboratory capability is used to characterize laboratory performance and method detection limits.

9.2.1 Method detection limit (MDL)—The method detection limit should be established for total solids using the QC spiking solution (Section 7.2). To determine MDL values, take seven replicate aliquots of the diluted QC spiking solution and process each aliquot through each step of the analytical method. Perform all calculations and report the concentration values in the appropriate units. MDLs should be determined every year or whenever a modification to the method or analytical system is made that will affect the method detection limit.

9.2.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and accuracy, the analyst shall perform the following operations:

9.2.2.1 Prepare four samples by diluting the QC spiking solution (Section 7.2) to 1-5 times the MDL. Using the procedures in Section 11, analyze these samples for total solids.

9.2.2.2 Using the results of the four analyses, compute the average percent recovery (\bar{x}) and the standard deviation (s , Equation 1) of the percent recovery for total solids.

Equation 1

$$s = \sqrt{\frac{\sum x^2 - \frac{(\sum x)^2}{n}}{n - 1}}$$

Where:

n = number of samples

x = % recovery in each sample

s = standard deviation

9.2.2.3 Compare s and \bar{x} with the corresponding limits for initial precision and recovery in Table 2 (to be determined in validation study). If s and \bar{x} meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or \bar{x} falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem, and repeat the test.

9.3 Laboratory blanks

9.3.1 Prepare and analyze a laboratory blank initially (i.e. with the tests in Section 9.2) and with each analytical batch. The blank must be subjected to the same procedural steps as a sample, and will consist of approximately 25 g of reagent water.

9.3.2 If material is detected in the blank at a concentration greater than the MDL (Section 1.3), analysis of samples must be halted until the source of contamination is eliminated and a new blank shows no evidence of contamination. All samples must be associated with an uncontaminated laboratory blank before the results may be reported for regulatory compliance purposes.

9.4 Ongoing precision and recovery

9.4.1 Prepare an ongoing precision and recovery (OPR) solution identical to the IPR solution described in Section 9.2.2.1.

9.4.2 An aliquot of the OPR solution must be analyzed with each sample batch (samples started through the sample preparation process (Section 11) on the same 12-hour shift, to a maximum of 20 samples).

9.4.3 Compute the percent recovery of total solids in the OPR sample.

9.4.4 Compare the results to the limits for ongoing recovery in Table 2 (to be determined in validation study). If the results meet the acceptance criteria, system performance is acceptable and analysis of blanks and samples may proceed. If, however, the recovery of total solids falls outside of the range given, the analytical processes are not being performed properly. Correct the problem, reprepare the sample batch, and repeat the OPR test. All samples must be associated with an OPR analysis that passes acceptance criteria before the sample results can be reported for regulatory compliance purposes.

9.4.5 Add results that pass the specifications in Section 9.4.4 to IPR and previous OPR data. Update QC charts to form a graphic representation of continued laboratory performance. Develop a statement of laboratory accuracy for each analyte by calculating the average percent recovery (R) and the standard deviation of percent recovery (SR). Express the accuracy as a recovery interval from $R-2SR$ to $R+2SR$. For example, if $R=05\%$ and $SR=5\%$, the accuracy is 85-115%.

9.5 Duplicate analyses

9.5.1 Ten percent of samples must be analyzed in duplicate. The duplicate analyses must be performed within the same sample batch (samples whose analysis is started within the same 12-hour period).

9.5.2 The total solids of the duplicate samples must be within 10% of the solids determination.

10.0 Calibration and Standardization

- 10.1** Calibrate the analytical balance at 2 mg and 1000 mg using class "S" weights.
- 10.2** Calibration shall be within $\pm 10\%$ (i.e. ± 0.2 mg) at 2 mg and $\pm 0.5\%$ (i.e. ± 5 mg) at 1000 mg. If values are not within these limits, recalibrate the balance.
- 10.3** Place a 50 g weight and a 2 mg weight on the balance. Verify that the balance reads $50.002 \pm 10\%$ (i.e. ± 0.2 mg)

11.0 Procedure

11.1 Preparation of evaporating dishes—Heat dishes and watch glasses at 103°C to 105°C for 1 hour in an oven. Cool and store the dried equipment in a desiccator. Weigh each dish and watch glass prior to use (record combined weight as " W_{dish} ").

11.2 Preparation of samples

11.2.1 Fluid samples—If the sample contains enough moisture to flow readily, stir to homogenize, place a 25 to 50 g sample aliquot on the prepared evaporating dish. If the sample is to be analyzed in duplicate, the mass of the two aliquots may not differ by more than 10%. Spread each sample so that it is evenly distributed over the evaporating dish. Cover each sample with a watch glass, and weigh (record weight as " W_{sample} "). Evaporate the samples to dryness on a steam bath.

NOTE: Weigh wet samples quickly because wet samples tend to lose weight by evaporation. Samples should be weighed immediately after aliquots are prepared.

11.2.2 Solid samples—If the sample consists of discrete pieces of solid material (dewatered sludges, for example), take cores from each piece with a No. 7 cork borer or pulverize the entire sample coarsely on a clean surface by hand, using rubber gloves. Place a 25 to 50 g sample aliquot of the pulverized sample on the prepared evaporating dish. If the sample is to be analyzed in duplicate, the mass of the two aliquots may not differ by more than 10%. Spread each sample so that it is evenly distributed over the evaporating dish. Cover each sample with a watch glass, and weigh (record weight as " W_{sample} ").

11.3 Dry the samples at 103°C to 105°C for a minimum of 12 hours, cool to balance temperature in an individual desiccator containing fresh desiccant, and weigh. Heat the residue again for 1 hour, cool it to balance temperature in a desiccator, and weigh. Repeat this heating, cooling, desiccating, and weighing procedure until the weight change is less than 5% or 50 mg, whichever is less. Record the final weight as " W_{total} ".

NOTE: It is imperative that dried samples be weighed quickly since residues often are very hygroscopic and rapidly absorb moisture from the air. Samples must remain in the dessicator until the analyst is ready to weigh them.

12.0 Data Analysis and Calculations

12.1 Calculate the % solids or the mg solids/kg sample for total solids (Equation 2).

Equation 2

$$\% \text{ total solids} = \frac{W_{\text{total}} - W_{\text{dish}}}{W_{\text{sample}} - W_{\text{dish}}} * 100$$

or

$$\frac{\text{mg total solids}}{\text{kg sludge}} = \frac{W_{\text{total}} - W_{\text{dish}}}{W_{\text{sample}} - W_{\text{dish}}} * 1,000,000$$

Where:

W_{dish} = Weight of dish (mg)

W_{sample} = Weight of wet sample and dish (mg)

W_{total} = Weight of dried residue and dish (mg)

12.2 Sample results should be reported as % solids or mg/kg to three significant figures. Report results below the ML as < the ML, or as required by the permitting authority or in the permit.

13.0 Method Performance

13.1 Method performance (MDL and quality control acceptance criteria) will be determined during the multi-lab validation of this method.

13.2 Total solids duplicate determinations must agree within 10% to be reported for permitting purposes. If duplicate samples do not meet this criteria, the problem must be discovered and the sample must be run over.

14.0 Pollution Prevention

14.1 Pollution prevention details are given in Section 14 of Method 1688.

15.0 Waste Management

15.1 Waste management details are given in Section 15 of Method 1688.

16.0 References

- 16.1** "Standard Methods for the Examination of Water and Wastewater," 18th ed. and later revisions, American Public Health Association, 1015 15th Street NW, Washington, DC 20005. 2-59: Section 2540 G (Total, Fixed, and Volatile Solids in Solid and Semisolid Matrices), 1992.
- 16.2** U.S. Environmental Protection Agency, 1992. Control of Pathogens and Vector Attraction in Sewage Sludges. Publ 625/R-92/013. Office of Research and Development, Washington, DC.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

- 17.1** Tables containing method requirements for QA/QC will be added after the validation study has been performed.